



Effect of copper surface area and acidic sites to intrinsic catalytic activity for dimethyl ether synthesis from biomass-derived syngas

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ARTICLE INFO

Article history:

Received 21 April 2012

Received in revised form 8 June 2012

Accepted 28 June 2012

Available online 4 July 2012

Keywords:

Dimethyl ether

Biomass-derived syngas

Bifunctional catalyst

Copper surface area

Acidic site

Intrinsic activity (TOF)

ABSTRACT

The crucial effects of copper surface area and acidic sites to intrinsic catalytic activity on the bifunctional catalysts such as Cu–ZnO/Al₂O₃ and Cu–ZnO–Al₂O₃/Zr-modified ferrierite catalysts have been investigated to find out the correlation between these two characteristics for the direct synthesis of dimethyl ether (DME) from biomass-derived syngas. The well-dispersed copper particles with a high reducibility as well as a large amount of weak acidic sites on bifunctional catalysts are responsible for their high catalytic performance. The high activity for methanol synthesis could be obtained by designing a high surface area of metallic copper with a low aggregation character, however, the quantity of the acidic sites on solid-acid components is also crucial factor for a high DME yield than the surface area of copper, which could be obtained by preparing proper bifunctional catalysts. It is mainly due to the fast reaction rate of methanol dehydration to DME compared to CO hydrogenation to methanol. The two important characteristics of the metallic surface area of copper and the amount of acidic sites are well correlated with the intrinsic catalytic activity on this consecutive reaction. The intrinsic activity for the direct DME synthesis from syngas on bifunctional catalysts initially decreases and maintains at constant value with the increase of the values of the copper surface area multiplied by the amount of acidic site.

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1. Introduction

The dimethyl ether (DME) synthesis from syngas, which could be derived from coal, biomass and natural gas, is one of the interesting methods to produce a renewable clean energy. Especially, biomass-derived H₂-deficient and CO₂-abundant syngas [1,2] has been getting more attendance recently for the synthesis of DME, since DME is an interesting renewable energy source by replacing it with a liquefied petroleum gas with a high potential to minimize the emissions of CO₂ and NO_x into the atmosphere by decreasing a global warming problem [3]. The commercial processes to produce DME from syngas generally involves two steps; the first step is to synthesize methanol by hydrogenation of CO and/or CO₂ on Cu–ZnO-based catalysts and the second step is to produce DME by the dehydration of methanol on the solid acid catalysts like γ -Al₂O₃ or modified zeolites [4–6]. Recently, a great emphasis has been laid on the development of a single-step process for the direct synthesis of DME from syngas using an efficient bifunctional catalyst which contains the above mentioned two functionalities [7–11].

The catalytic performance on the bifunctional catalysts is well explained from many aspects; for example, dispersion of copper particles, acidic properties of solid-acid catalysts, the adsorption behavior of H₂O and CO₂, and so on [12–15]. To enhance the DME production, it is important to design the catalyst possessing a high surface area of metallic copper and to optimize the acidic properties such as their quantities and strengths by modifying the solid-acid catalysts with promoters [16–18]. In addition, the reducibility of copper oxides and acidic properties on the bifunctional catalysts are found to be influenced by many factors such as the pH of precipitation solution, and the aging duration and its temperature [5]. Generally, the efficient bifunctional catalysts could be prepared by changing the precipitation conditions [6–9], stabilization of active copper species by adding promoters [9], modification of surface acidity of solid-acid catalyst by adding metals on zeolites such as ZSM-5 [19] and so on.

In the present paper, we shortly reviewed the effects of copper surface area and the amount of acidic sites to catalytic performance during the single-step synthesis of DME from biomass-derived syngas on the bifunctional catalysts. The catalytic performance and its physicochemical properties are affected by copper surface area and the amount of acidic sites as mentioned in our previous works [20–22], and it is also significantly depending on the metallic surface area of copper particles and the acidic properties

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of the bifunctional catalysts. Therefore, we have tried to find out some simple correlations between catalyst properties and intrinsic activity for the direct synthesis of DME from biomass-derived syngas, which is composed of two consecutive reactions such as CO hydrogenation to methanol on Cu-ZnO catalyst and dehydration of methanol to DME on acidic sites such as Al_2O_3 or Zr-modified H-ferrierite. The reasons for the selection of such solid-acid catalysts are to elucidate the general correlation of the metallic copper surface area and the amount of acidic site for intrinsic catalytic activity on the bifunctional catalysts, because these selected solid acid catalysts showed a large variation of catalytic activity and a high DME selectivity with a small coke formation.

2. Experimental

2.1. Preparation of bifunctional catalysts

2.1.1. Preparation of Cu-ZnO/ Al_2O_3 catalyst

The solid acid catalyst of $\gamma\text{-Al}_2\text{O}_3$ for methanol dehydration having a surface area of $412.8\text{ m}^2/\text{g}$ was prepared by sol-gel method, which is precisely described in our previous work [23]. The bifunctional catalysts were subsequently prepared by co-precipitation and deposition method in a $\gamma\text{-Al}_2\text{O}_3$ slurry at 70°C with a final pH of around 7 using different copper precursors such as copper acetate, nitrate or chloride and zinc acetate precursor by using a Na_2CO_3 precipitant. The weight ratio of $\text{CuO}/\text{ZnO}/\gamma\text{-Al}_2\text{O}_3$ is fixed at 62.5/20.8/16.7. Then precipitate was further aged for 3 h at 70°C followed by calcination at 300°C for 5 h. The bifunctional catalysts are denoted as CZA(M), where C, Z, and A represent CuO, ZnO, and $\gamma\text{-Al}_2\text{O}_3$ respectively, and M denotes type of copper precursors, i.e. copper acetate (A), nitrate (N) and chloride (C) as mentioned in our previous work [20].

2.1.2. Preparation of Cu-ZnO- Al_2O_3 /Zr-ferrierite catalyst

The bifunctional Cu-ZnO- Al_2O_3 /Zr-ferrierite catalysts (denoted as CZA/ZrFER) consisting 7:3 weight ratio of CuO-ZnO- Al_2O_3 to Zr-modified ferrierite (denoted as ZrFER) were prepared by a coprecipitation and deposition method of Cu-ZnO- Al_2O_3 components in a slurry of Zr-modified H-ferrierite using copper acetate monohydrate, zinc acetate dihydrate and aluminum nitrate precursors with different precipitants. On the bifunctional CZA/Zr-FER catalyst, a metal oxide composition was around 50 wt%CuO, 40 wt%ZnO, and 10 wt% Al_2O_3 . The acidic component of ZrFER was prepared by loading 3 wt% of Zr metal with a precursor of $\text{ZrCl}_2\cdot 0.8\text{H}_2\text{O}$ on H-ferrierite (Si/Al = 25 provided by Zeolyst) by incipient wetness impregnation method. The H-ferrierite has a surface area of $364\text{ m}^2/\text{g}$ and a pore volume of $0.13\text{ cm}^3/\text{g}$. The acidic catalyst was calcined at 400°C for 5 h after Zr impregnation. Then the precipitate was dried in an oven at 110°C for above 12 h and subsequently calcined at 350°C for 5 h in air flow. The catalysts are denoted as CZA/ZrFER(P), where CZA stands for the Cu-ZnO- Al_2O_3 component, ZrFER for a Zr-modified H-ferrierite at a fixed weight ratio of 3 wt%Zr on H-ferrierite. The P in bracket denotes the alkali metal ion K or NH_3 for K_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$ as precipitants.

The ZrFER was further prepared by loading a different Zr content from 0 to 5 wt% by impregnation method using Na_2CO_3 as a precipitant at a pH of around 7, and it is further digested at 70°C for 3 h. The bifunctional catalysts are denoted as CZA/ZrFER(X), where CZA stands for Cu-ZnO- Al_2O_3 component and ZrFER for Zr-modified ferrierite. The X in the bracket also denotes a Zr content such as 0, 1, 3 and 5 wt% based on the 100 wt% of bare H-ferrierite as mentioned in our previous works [21,22].

2.2. Catalytic activity measurement

The catalytic performance was tested in a fixed-bed tubular reactor (12.7 mm O.D.) with a catalyst loading of 1.0 g and its

particle size of $\sim 100\text{ }\mu\text{m}$. Prior to reaction, the bifunctional catalysts were activated (reduced) in a flow containing 5% H_2 balanced with helium at 250°C for 4 h. The synthesis gas and argon, which was used as an internal standard, was simultaneously fed into the reactor, and molar feed composition of $\text{CO}/\text{CO}_2/\text{H}_2 = 41/21/38$ (the biomass-derived model synthesis gas) was adopted. The reaction was carried out for above 15 h on stream at the following reaction conditions; $T = 250^\circ\text{C}$, $P = 5.0\text{ MPa}$ and space velocity (SV) = $4000\text{ ml/g}_{\text{cat}}/\text{h}$ for CZA catalysts and $T = 250^\circ\text{C}$, $P = 4.0\text{ MPa}$ and $\text{SV} = 5500\text{ ml/g}_{\text{cat}}/\text{h}$ for CZA/ZrFER catalysts as precisely mentioned in our previous works [20–22]. The CO conversion and products distribution were obtained from the average values after 12 h on stream at steady-state. The products were analyzed using an on-line gas chromatograph (Younglin GC, YL6100) using a thermal conductivity detector (TCD) to analyze Ar, CO and CO_2 and a flame-ionized detector (FID) to analyze hydrocarbons.

2.3. Catalyst characterization

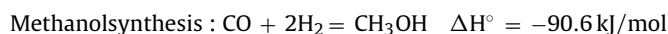
BET surface area, pore volume and average pore diameter on the fresh bifunctional catalysts were determined by N_2 sorption method using Micromeritics ASAP2400 apparatus at liquid- N_2 temperature (-196°C). The calcined catalysts were degassed at 300°C in a He flow for 4 h before taking the measurement.

To carry out temperature-programmed reduction (TPR) experiments, the bifunctional catalysts were pretreated with a He flow up to 250°C for 2 h to remove the adsorbed water and it is followed by cooling to 50°C . The 5% H_2/He mixture was introduced to the catalyst bed at a flow rate of 30 ml/min , with a heating rate of 10°C/min up to 500°C . The effluent gas was passed through a molecular sieve to remove water formed, and it was analyzed by GC equipped with TCD. Temperature-programmed desorption of ammonia (NH_3 -TPD) was performed in order to determine the surface acidity on the fresh bifunctional catalysts. Approximately 0.1 g of the bifunctional catalyst was initially flushed with a He flow at 250°C for 2 h. The catalyst was cooled to 100°C and it was saturated with pure NH_3 gas. After NH_3 exposure, the catalyst was purged with a He flow until it reached equilibrium, then allowed TPD experiment in the range of $100\text{--}700^\circ\text{C}$ at a heating rate of 10°C/min with TCD.

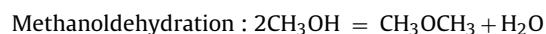
The surface area of metallic copper on bifunctional catalysts before and after reaction was measured by N_2O titration method. Prior to the N_2O titration, the bifunctional catalyst was reduced at 250°C for 4 h with 5% H_2/N_2 flow. The consumption of N_2O and the release of N_2 on metallic copper sites ($\text{N}_2\text{O} + 2\text{Cu} = \text{Cu}_2\text{O} + \text{N}_2$) were analyzed by TCD. The surface area of metallic copper was calculated by assuming $1.46 \times 10^{19}\text{ Cu atoms/m}^2$ with a molar ratio of 0.5 for $\text{N}_2\text{O}/\text{Cu}_s$ (Cu atom on surface) [24]. To support the results of N_2O titration, powder X-ray diffraction (XRD) patterns on fresh and used bifunctional catalysts were also carried out on Rigaku diffractometer using $\text{Cu K}\alpha$ radiation in order to identify the phases of the bifunctional catalysts and their particle size. Especially, the particle size of metallic copper after reaction was measured after the passivation of bifunctional catalysts with 1.0 vol% O_2 balanced with N_2 to minimize the abrupt oxidation of metallic copper in air exposure. The more detailed experimental conditions, the calculation method of copper particle size and characterization method are explained in our previous works [13,15,20–22].

3. Results and discussion

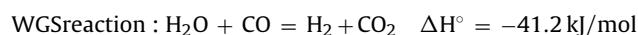
The major reactions involved in direct DME synthesis from syngas could be categorized as following three reactions;



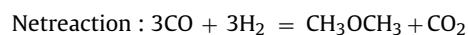
(1)



$$\Delta H^\circ = -23.4 \text{ kJ/mol} \quad (2)$$



(3)



$$\Delta H^\circ = -245.8 \text{ kJ/mol} \quad (4)$$

The changes of enthalpies of each reaction indicate that the formation of DME (Eq. (4)) reveals the high exothermic reaction thermodynamically compared to that of other reactions (Eqs. (1)–(3)). The DME formation in direct method is more favorable due to the surplus hydrogen production during the reaction because water-gas shift (WGS) reaction is favorable through the facile reaction of CO with water formed. The main advantage of direct synthesis of DME from the biomass-derived H_2 -deficient and CO_2 -abundant syngas lies in surpassing the equilibrium limitation involved in CO hydrogenation to methanol with the help of surplus hydrogen supply. The hydrogen formed by WGS reaction generates hydrogen-rich environments, which are suitable for obtaining high CO conversion. Therefore, CO conversion is much higher in direct DME synthesis than that of methanol synthesis reaction, especially using biomass-derived syngas which is characterized as a low H_2/CO ratio below 1. The product distribution is also largely altered according to the extent of WGS activity [3,8,25]. Therefore, two different bifunctional catalysts were newly employed to elucidate the effects of copper surface area and acidic properties to intrinsic catalytic activity, such as CZA and CZA/ZrFER catalysts by using the biomass-derived model syngas in this consecutive direct DME synthesis reaction.

3.1. Characteristics of bifunctional catalysts

3.1.1. Physicochemical properties

BET surface area, pore volume and average pore diameter on CZA bifunctional catalysts significantly vary according to the type of copper precursors as summarized in Table 1. The surface area is found to be in the range of 89.8–127.8 m^2/g , and CZA(N) catalyst has the highest surface area of 127.8 m^2/g with the following trend; $\text{CZA(N)} > \text{CZA(A)} > \text{CZA(C)}$. Although no significant correlation between surface area and catalytic performance on the bifunctional catalysts has been reported, surface area of catalysts could alter significantly the copper surface area [16,21,22,26], which could largely alter the catalytic performance on methanol synthesis reaction from syngas.

The characteristics of CZA/ZrFER catalysts are also included Table 1. The surface area of CZA/ZrFER(NH_3) shows a large surface area of 240.4 m^2/g and small average pore diameter of 12.8 nm. The surface area of CZA/ZrFER(0) is found to be 134.0 m^2/g and it decreased to 120.8 m^2/g on CZA/ZrFER(3) catalyst. The decrease of surface area from 364 m^2/g of bare H-ferrierite is attributed to the possible pore blockage by CZA component deposition and Zr modification during CZA/ZrFER catalyst preparation step. The large pore volume of 0.56 cm^3/g , and moderate average pore diameter and surface area of 32.2 nm and 120.8 m^2/g respectively were observed on CZA/ZrFER(3). Although the larger average pore diameter is generally beneficial for obtaining a high catalytic activity by the easy mass-transfer effects of reactants and products, the amount of acid sites and the copper surface area should be carefully considered on bifunctional catalyst to explain the variation of intrinsic catalytic

Table 1

Textural properties and composition of the bifunctional catalysts [20–22].

Notation ^a	N ₂ sorption method		
	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
CZA(A)	111.5	0.38	12.1
CZA(N)	127.8	0.49	11.9
CZA(C)	89.8	0.57	24.0
CZA/ZrFER(0)	134.0	0.33	26.1
CZA/ZrFER(1)	124.0	0.35	33.1
CZA/ZrFER(3)	120.8	0.56	32.2
CZA/ZrFER(5)	130.9	0.53	26.0
CZA/ZrFER(K)	190.7	0.72	24.9
CZA/ZrFER(NH_3)	240.4	0.53	12.8

^a The bifunctional catalysts are denoted as CZA(M), where C, Z, and A represent CuO, ZnO, and $\gamma\text{-Al}_2\text{O}_3$ respectively, and M denotes the type of copper precursors i.e. copper acetate (A), nitrate (N) and chloride (C) precursor. The catalysts are also denoted as CZA/ZrFER(P), where ZrFER stands for Zr-modified ferrierite and P in bracket denotes the type of precipitants of K_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$ respectively. The catalysts denoted as CZA/ZrFER(X) represent that X in bracket denotes Zr content such as 0, 1, 3 and 5 wt% based on the 100 wt% of bare ferrierite.

activity [13–16,20–22]. The high DME selectivity is strongly related with the extent of acid sites as well as the surface area of metallic copper, which is the crucial first step for methanol synthesis.

3.1.2. Reducibility of copper oxides by TPR experiments

The catalytic performance on the bifunctional catalysts strongly relies on reducibility of the copper particles as reported

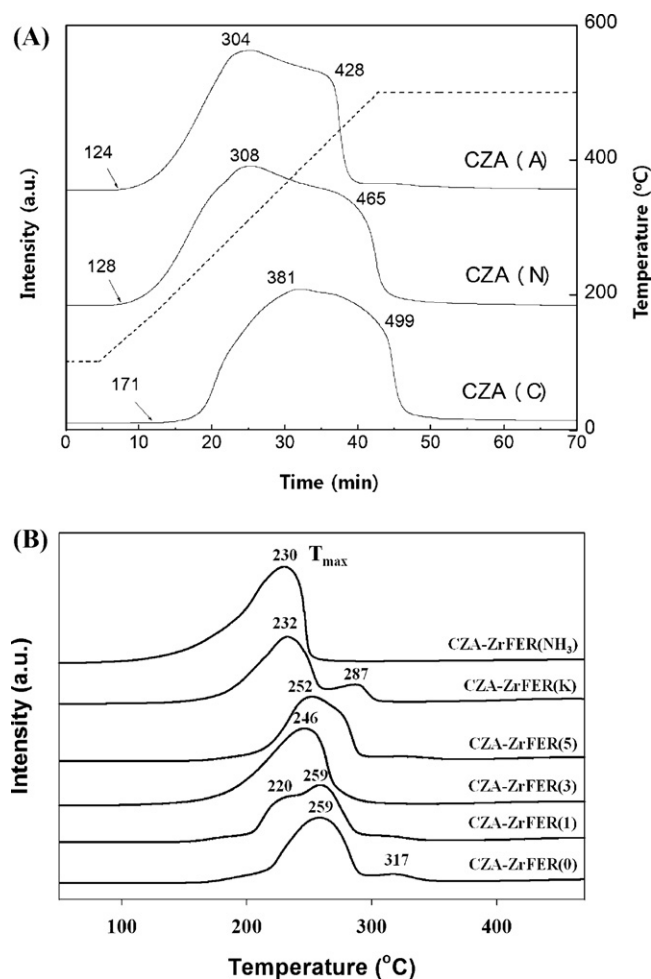


Fig. 1. TPR profiles on the bifunctional catalysts [20–22]. CZA catalysts (A); CZA/ZrFER catalysts (B).

previously [13–16,20–22,26]. As shown in Fig. 1(A) on CZA catalysts, TPR profiles on CZA catalysts exhibit only one broad reduction peak without showing any shoulder peak in the range of 100–500 °C, which implies the homogeneous distribution of CuO particles on CZA bifunctional catalysts. On CZA(A) catalyst, maximum reduction peak (T_{\max}) at around 304 °C is lower than the other two bifunctional catalysts, which also suggests the facile reducibility of CuO on CZA(A) catalyst. In contrast, the reduction on CZA(C) was observed at T_{\max} around 381 °C and it was not fully reduced even at 500 °C. The different reduction behaviors according to the copper precursors suggest that the reducibility is in the order of CZA(A) > CZA(N) > CZA(C) catalyst.

As shown in Fig. 1(B), all CZA/ZrFER catalysts were easily reduced below 300 °C compared to CZA catalysts with a single stage reduction step except for CZA/ZrFER(0) catalyst. The satellite peak at around 317 °C on CZA/ZrFER(0) catalyst suggests a heterogeneous distribution of CZA components with a strong interaction with ferrierite. With the increase of Zr content up to 3 wt% in CZA/ZrFER catalysts, the maximum reduction peak shifted to lower temperature from 259 to 246 °C. The CZA/ZrFER(3) catalyst reveals one sharp reduction peak at T_{\max} of 246 °C and the others show one reduction peak with a shoulder peak above 250 °C. The presence of shoulder peaks at high temperature also suggests a heterogeneous distribution of copper oxides, especially on CZA/ZrFER(1) and CZA/ZrFER(5) catalysts. The reduction profiles on CZA/ZrFER catalyst prepared from different precipitants are also shown in Fig. 1(B), and the temperature shifted to lower temperature (from 246 °C for CZA/ZrFER(3) to 230 °C for CZA/ZrFER(NH₃)). The intermediate value on CZA/ZrFER(K) catalyst was observed, and a shoulder peak at higher temperature of 287 °C was also observed which indicates that the complete reduction of copper oxides is rather difficult compared to other catalysts. A considerable decrease in the reduction temperature on CZA/ZrFER(NH₃) catalyst implies the formation of a more easily reducible copper oxides. The formation of homogeneous microstructure with a similar chemical composition plays an important role to obtain a high surface area of metallic copper on the Cu-ZnO-Al₂O₃ catalyst [27]. Therefore, the homogeneous distribution of copper oxides could be effectively explained by considering the reduction patterns during TPR experiments and the presence of shoulder peaks at a high temperature represents the heterogeneous distribution of copper oxides in bifunctional catalysts, especially on CZA/ZrFER(1), CZA/ZrFER(5) and CZA/ZrFER(K) catalysts.

3.1.3. Acidity measurement from NH₃-TPD experiments

The summarized results of NH₃-TPD on the bifunctional catalysts are represented in Table 2 to illustrate the effects of surface acidity to the activity of methanol dehydration to DME. The desorption patterns of NH₃ display the distinguishable three peaks, in the regions of 100–250 °C (T_1), 250–450 °C (T_2) and above 450 °C (T_3). The different NH₃ desorption behaviors on the bifunctional catalysts compared to bare γ -Al₂O₃ or H-ferrierite are mainly induced from the deposition of CuO-ZnO-(Al₂O₃) particles on solid-acid surface [23]. According to our previous results [13–16,20–22], T_1 corresponds to the acidic sites attributed to the solid-acid catalyst matrix alone, and T_2 is due to the presence of catalytic species on the surface. Consequently, both T_1 and T_2 peaks could be assigned to the active sites for methanol dehydration reaction. The concentration of the acidic sites for T_1 and T_2 peaks are approximately 2.338, 1.521 and 1.356 mmol NH₃/g for CZA(A), CZA(N) and CZA(C) catalyst, respectively. The larger quantity of the acidic sites on CZA(A) catalysts could be responsible for its higher methanol dehydration activity.

The variation of acidity on CZA/ZrFER catalysts is also summarized in Table 2. The desorption peak assigned to T_1 is a characteristic peak for weak acidic site of H-ferrierite and the

remaining peaks (T_2 and T_3) are attributed to CuO-ZnO-Al₂O₃ component present on the surface of H-ferrierite and the desorption of water from the frameworks of metal oxides respectively [28]. Interestingly, the total acidic sites ($T_1 + T_2$) steadily decreases to the value of 1.040 on CZA/ZrFER(5) from 1.337 mmol NH₃/g on CZA/ZrFER(0) catalyst. The amount of weak acidic sites of T_1 is minimized on CZA/ZrFER(3) around 0.209 mmol NH₃/g catalyst, which showed a high catalytic performance. The abundant presence of acid sites on Zr-modified ferrierite itself (3 wt% Zr on Ferrierite) is possibly a manifestation of high dispersion of CuO-ZnO-Al₂O₃ particles during coprecipitation and deposition step in a slurry of ZrFER zeolite. It further alters the amount of acid sites on CZA/ZrFER catalysts by blocking the surface acid sites of H-ferrierite as mentioned by Flores and da Silva [29]. Furthermore, DME selectivity on CZA/ZrFER catalyst is related with the amount of acidic sites assigned to T_1 and T_2 desorption peaks. Therefore, CZA/ZrFER(3) catalyst possessing a moderate amount of acidic sites with a small amount of strong acidic sites is responsible for showing a high CO conversion and DME selectivity due to the high dispersion of Cu-ZnO-Al₂O₃ and large amount of acidic sites. In addition, on CZA/ZrFER catalysts prepared by different precipitants, the residual ions deposited from precipitating agents also influenced acidic properties of bifunctional catalysts. Among three precipitating agents, the catalyst prepared by using K₂CO₃ showed the lowest value for weak and medium acidity (around 0.979 mmol/g), whereas that from (NH₄)₂CO₃ showed the highest value of 2.181 mmol/g. The CZA/ZrFER(NH₃) also shows the highest number of total acidic sites. The reason for CZA/ZrFER(NH₃) catalyst to exhibit the highest activity can be attributed to retain a larger quantity of weak and medium acidity. Therefore, the surface acidic sites assigned to T_1 and T_2 desorption peaks on the bifunctional catalysts are selectively considered to correlate with intrinsic catalytic activity for methanol dehydration to DME.

3.1.4. Particle size and surface area of metallic copper

To verify particle sizes and metallic surface area of copper species on the fresh and used bifunctional CZA and CZA/ZrFER catalysts, both XRD and N₂O titration method were employed. The particle size of CuO and metallic copper (Cu⁰) are calculated from the Scherrer's equation using the values of full width at half maximum (FWHM) at $2\theta = 35.6^\circ$ for CuO and $2\theta = 43.3^\circ$ for Cu⁰, and the results are included in Table 2. The particle size of CuO on fresh catalysts is not altered significantly according to the type of copper precursors and the type of solid-acid catalysts. The particle size CuO remains in the range of 10.6–12.3 nm on all bifunctional catalysts. However, the particle size of metallic copper after reaction drastically changes due to the different reducibility of CuO and its different sintering phenomena by showing in the range of 11.9–43.2 nm, especially larger on CZA catalysts than CZA/ZrFER catalysts. The variation of particle size on CZA/ZrFER catalysts before and after reaction is not significant compared to that of CZA catalysts, however, the particle size is slightly increased after reaction.

As shown in Table 2, the metallic copper surface area measured by N₂O titration is found to be in the range of 0.45–14.17 m²/g on the fresh bifunctional catalysts. The large surface area of metallic copper on CZA catalysts was observed around 14.17 m²/g on fresh CZA(N) catalyst, and medium surface area around 5.49 m²/g was observed on CZA(A) catalyst. The observed smallest surface area of metallic copper at around 0.45 m²/g on CZA(C) catalyst was possible attributed to the difficult reducibility and the formation of larger CuO particles due to the possible presence of residual chloride ions. CZA/ZrFER(3) catalyst also shows larger surface area of 3.90 m²/g. With the increase of acidity of Zr-modified ferrierite, the dispersion of CZA component increases and it results in higher metallic surface area of copper species. The catalytic

Table 2

Acidity, particle size and metallic copper surface area on the bifunctional catalysts [20–22].

Notation	Acidic sites (mmol NH ₃ /g) ^a			Particle size of CuO and Cu ⁰ (nm) ^b		Cu surface area (m ² /g _{copper}) ^c		[Cu surface area (after)] × [acidic site (total)]
	T ₁ (<250 °C)	T ₂ (<450 °C)	Total	CuO (before)	Cu ⁰ (after)	Before reaction	After reaction	
CZA(A)	0.440	1.898	2.338	10.9	28.5	5.49	3.79	8.86
CZA(N)	0.421	1.100	1.521	10.6	16.4	14.17	4.45	6.77
CZA(C)	0.129	1.227	1.356	11.3	43.2	0.45	0.11	0.15
CZA/ZrFER(0)	0.211	1.126	1.337	11.5	12.5	3.49	0.90	1.20
CZA/ZrFER(1)	0.223	1.090	1.313	11.4	13.8	3.11	1.80	2.36
CZA/ZrFER(3)	0.209	0.959	1.168	11.8	11.9	3.90	4.23	4.94
CZA/ZrFER(5)	0.258	0.782	1.040	12.3	13.9	1.54	0.72	0.75
CZA/ZrFER(K)	0.220	0.759	0.979	–	–	4.59	2.64	2.58
CZA/ZrFER(NH ₃)	0.649	1.532	2.181	–	–	13.50	5.74	12.52

^a The desorption peaks from NH₃-TPD was separated in the regions of 100–250 °C (T₁), 250–450 °C (T₂) and above 450 °C (T₃).^b The particle size of copper oxides before and after reaction was calculated from FWHM of XRD diffraction peaks at 2θ = 35.6° for CuO for the catalyst before reaction and 2θ = 43.3° for metallic copper (Cu⁰) for the catalyst after reaction.^c The copper surface area (defined as S_{Cu} = exposed metallic copper area (m²/g) of sample) before and after reaction was measured by the N₂O surface titration method.

performance indicates that the copper surface area and particle size are well correlated with the steady-state catalytic activity. Due to high surface area of around 4.23, 4.45 and 5.74 m²/g on the used CZA/ZrFER(3), CZA(N) and CZA/ZrFER(NH₃) catalysts respectively, the high catalytic performance was also observed on these bifunctional catalysts. Severe aggregation by sintering during reaction and partial oxidation of metallic copper species on CZA/ZrFER(0) and CZA/ZrFER(5) catalysts was observed and they eventually showed a low catalytic activity at steady-state. As shown in Table 2, the particle size calculated from XRD analysis is found to be in the range of 11.9–43.2 nm on the used bifunctional catalysts, and the variation is well supported by the results of N₂O titration. The catalyst deactivation of Cu-ZnO-based methanol synthesis catalysts are generally explained by the aggregation of copper particles at a high temperature and pressure to result in agglomeration of metallic copper even at the reaction conditions of methanol synthesis from the very beginning of reaction [30]. Many researchers have tried to design the thermally stable methanol synthesis catalysts by adding some promoters. The bifunctional catalysts for the direct DME synthesis from syngas are also easily deactivated by the sintering mechanism of copper particles and a concomitant loss of acidic sites by redispersion of copper which possibly blocks the acidic sites [13–16,20–22], and possible coke formation on catalyst surfaces and so on [31]. Even though the coke formation through the strong adsorption of methoxy intermediates on the metallic copper surfaces could also affect the catalyst deactivation rate [31], the sintering of copper particles could largely alters the catalyst deactivation by reducing active metallic copper surface area at the reaction conditions of small hydrocarbon formation. The surface area of metallic copper crucially acts as the active sites for methanol synthesis by CO hydrogenation.

3.2. Catalytic performance on bifunctional catalysts

The catalytic activity and product distribution at steady state are summarized in Table 3 [20–22]. The catalytic activities on CZA catalysts in terms of CO conversion and DME yield are higher on CZA(A) catalyst at around 65.8% and 32.2% respectively, and they are lower on CZA(C) catalyst at around 1.7% and 0.1% respectively. The reaction rate for CO consumption, which is defined as the reacted CO mol/g_{cat}/h, is summarized in Table 3. The highest value on CZA(A) catalyst of 0.0392 and lowest value on CZA(C) catalyst of 0.001 were observed. The catalytic activity and product distribution on CZA/ZrFER catalysts are also presented in Table 3 and DME selectivity is generally higher on CZA/ZrFER compared to CZA bifunctional catalysts. The introduction of Zr-modified ferrierite showed positive effects with respect to catalyst stability and DME selectivity. The catalytic activity is maximized on CZA/ZrFER(3) catalyst with

CO conversion of 49.0% and DME selectivity of 58.2%. The activity is further increased on CZA/ZrFER(NH₃) catalyst up to 62.9% of DME selectivity. The reaction rate for CO consumption on CZA/ZrFER catalysts is found to be in the range of 0.0178–0.0354 and the rate is found to be larger on CZA/ZrFER(3) and CZA/ZrFER(NH₃) catalysts. The reaction rate is simultaneously depending on CO hydrogenation to methanol and subsequent dehydration of methanol to DME on the bifunctional catalysts. Therefore, to verify the intrinsic catalytic activity, the turnover frequency (TOF, s^{−1}), which is defined as the reacted CO molecule/surface copper atom/s by using the results of copper surface area obtained from N₂O titration method on the used catalysts. As shown in Table 3, TOF values are found to be 0.118, 0.089 and 0.105 on CZA(A), CZA(N) and CZA(C) bifunctional catalyst respectively without a significant variation. The product distribution, particularly for the formation of hydrocarbons, is much greater on the CZA(C) catalyst due to the abundant presence of Cu²⁺ species, and it is the possible active sites for methanol or DME reforming reaction [13–16,20–22].

In addition, TOF values on CZA/ZrFER catalysts showed a minimum value of 0.79 on CZA/ZrFER(3) catalyst which showed highest CO conversion due to the higher metallic copper surface area of 4.23 m²/g and smaller particle size of 11.9 nm, and it showed a lower TOF value of 0.79. The TOF values on CZA/ZrFER catalysts are found to be in the range of 0.071–0.282 and they are inversely correlated with CO conversion and reaction rate as shown in Table 3. However, CO conversion on CZA/ZrFER catalysts is linearly correlated with copper surface area. It suggests that a high surface area of metallic copper is beneficial to obtain a high catalytic activity for methanol synthesis. Although the amount of extra-hydrogen produced by WGS reaction will be almost the same and the rate of methanol formation did not differ significantly, the faster consumption of methanol by dehydration is attributable to the higher CO conversion and DME selectivity. As reported by Blaszkowski and van Santen [32], the partial pressure of the formed methanol could enhance DME selectivity due to the lowest activation barrier for the pathway involving two methanol adsorption concomitantly. Therefore, the different TOF values and reaction rates could possibly suggest that the intrinsic activities on bifunctional catalysts are rather depending on the rate of methanol dehydration on acidic sites and the extent of methanol formation. Since the intrinsic rate (TOF) of methanol dehydration to DME is faster than that of methanol synthesis by CO hydrogenation [13,19], the high concentration of methanol on the active copper surfaces is responsible for a high intrinsic rate for the direct DME synthesis on CZA/ZrFER(3) and CZA/ZrFER(NH₃) catalysts, which showed the high metallic copper surface area. Therefore, the high production rate of DME on bifunctional catalysts could be significantly attributed to the high production rate of methanol with a high metallic copper surface

Table 3
CO conversion, reaction rate, TOF and the product distribution on the bifunctional catalysts^a [20–22].

Notation	CO conversion (mol%)	Reaction rate/ 10^{-2} (reacted CO mol/g _{cat} /h)	TOF/ 10^{-1} (reacted CO molecule/surface Cu atom/s) ^b	Product distribution (mol%)				Yield of DME (mol %)
				CH ₃ OH	DME	CO ₂	BP ^c	
CZA(A)	65.8	3.92	1.18	34.1	49.0	15.7	1.2	32.2
CZA(N)	58.1	3.46	0.89	48.1	32.3	18.2	1.4	18.8
CZA(C)	1.7	0.10	1.05	88.8	6.6	0.5	4.1	0.1
CZA/ZrFER(0)	30.4	1.81	2.30	42.8	28.7	27.9	0.6	8.7
CZA/ZrFER(1)	35.3	2.10	1.34	22.1	40.8	36.7	0.4	14.4
CZA/ZrFER(3)	49.0	2.92	0.79	7.8	58.2	33.7	0.3	28.5
CZA/ZrFER(5)	29.8	1.78	2.82	34.0	34.0	31.6	0.4	10.1
CZA/ZrFER(K)	40.8	2.43	1.05	27.7	37.5	33.4	1.4	15.3
CZA/ZrFER(NH ₃)	59.4	3.54	0.71	1.9	62.9	34.7	0.5	37.4

^a The catalytic performance test was carried out under following reaction conditions for 15 h on stream; $P=4.0\text{--}5.0$ MPa, $SV=4000\text{--}5500$ ml/g_{cat}/h, feed composition of CO/CO₂/H₂ = 41/21/38 and $T=250^\circ\text{C}$. The CO conversion and product distribution were obtained for steady-state average values after 12 h on stream.

^b The turnover frequency (TOF) is defined as the reacted CO molecule/surface copper atom/s by applying copper surface area after reaction.

^c Byproducts (BP) mainly include CH₄ and a trivial amount of C₂ hydrocarbons.

area and moderate amount of acidic sites. However, its intrinsic rate is suppressed by the reduced number of adjacent acid sites for the adsorption of two methanol molecules on the bifunctional catalysts, which could be suppressed by the deposition of small CZA particles on acidic sites. Additionally, the extra-hydrogen produced by WGS reaction accelerates the conversion of CO and this is also in the agreement with the observation of high CO₂ formation.

3.3. Correlation with copper surface area and acidic sites to intrinsic activity

The catalytic performance on the selected bifunctional catalysts [20–22] strongly depends on the surface area of metallic copper and the amount of acidic sites. To verify the effect of these two factors to intrinsic activity, the correlation of surface area of metallic copper and acidic sites to catalytic performance such as CO conversion and DME yield are represented in Fig. 2. In addition, the variations of TOF values and reaction rates are also displayed in Fig. 3. The metallic copper surface area on the used bifunctional catalysts is only taken into consideration to verify the catalytic activity at steady-state with the amount of acidic sites from NH₃-TPD results. In addition, to correlate surface area of metallic copper after reaction with the total amount of acidic sites assigned to the intensities of $T_1 + T_2$ peaks in NH₃-TPD to catalytic activity, the product of two properties [copper surface area (m²/g) \times amount of acidic sites (mmol NH₃/g)] was plotted with respect to the CO conversion and DME yield. The results are summarized in Fig. 2 and Table 2. Compared to the correlation of catalytic performance with copper surface area only as shown in Fig. 2(A), the correlation of catalytic performance with the surface area of metallic copper multiplied by the amount of acidic sites (Fig. 2(B)) is found to be better explained with a good estimation. The correlation shows a high coefficient of determination of R^2 ; for example, higher value of $R^2 = 0.9151$ for CO conversion with two parameters (copper surface area and acidic sites) estimation in Fig. 2(B) than that of $R^2 = 0.8862$ for CO conversion with one parameter (copper surface area) estimation in Fig. 2(A). Therefore, the catalytic activity is strongly related with metallic copper surface area as well as the amount of acidic sites together on this consecutive reaction of direct DME synthesis from syngas. With the increase of the product values of two properties (copper surface area \times amount of acidic sites), CO conversion and DME yield is found to be in the shape of inverse-exponential curve which is irrespective to the types of bifunctional catalysts such as CZA and CZA/ZrFER catalysts. In general, the overall reaction rate for the direct DME synthesis from syngas could be depending on the rate of methanol dehydration since the equilibrium conversion increased with the surplus hydrogen formed by WGS reaction during methanol dehydration step. As reported by Blaszkowski and

van Santen [32], the lowest activation barrier for the adsorption pathway of two contiguous methanol molecules is responsible for the facile formation of DME by methanol dehydration when compared to the methoxy formation from one methanol molecule adsorption. Therefore, the increased CO conversion with increasing

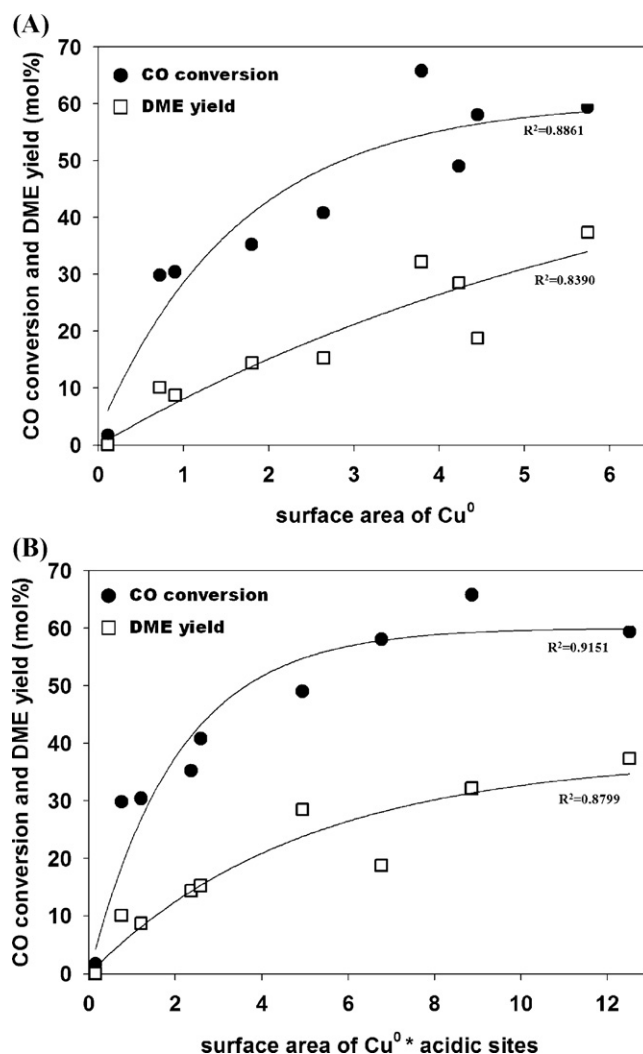


Fig. 2. Correlation of CO conversion and DME yield with copper surface area only (A), and catalytic activity with copper surface area (m²/g) multiplied by amount of acidic sites (mmol NH₃/g) (B).

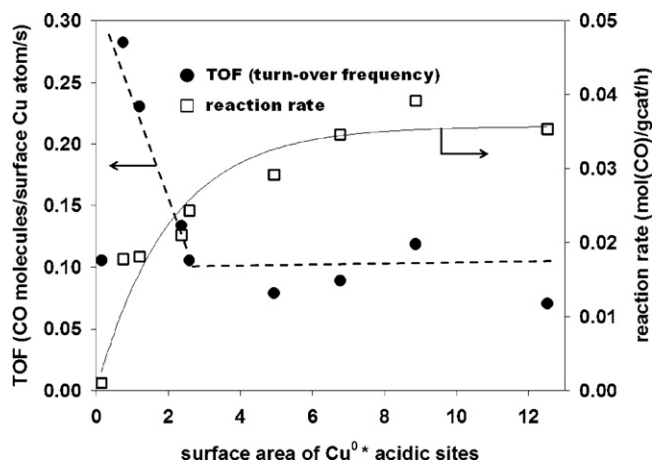


Fig. 3. Correlation of TOF values (reacted CO molecules/surface Cu atom/s) and reaction rates (reacted CO(mol)/gcat/h) with the values of copper surface area (m^2/g) multiplied by amount of acidic sites ($\text{mmol NH}_3/\text{g}$).

the product values of two properties (surface area of copper and acidic sites) upto ~ 6 could be possibly attributed to the increased formation of methanol by increasing copper surface area with a large amount of acidic sites. However, CO conversion is kept constant above 6 due to the possible blockage of acidic sites by CuO-ZnO-(Al_2O_3) particles. In addition, DME yield with respect to the product values of two properties as shown in Fig. 2(B) is steadily increased since the fast dehydration rate of methanol to DME.

The variations of TOF values and reaction rates with respect to the product of two properties also plotted in Fig. 3. Even though a larger amount of acidic sites with a proper amount of surface area of metallic copper on bifunctional catalyst seems to be beneficial to achieve a high DME yield due to the fast methanol dehydration rate to DME compared to that of CO hydrogenation to methanol. However, the reaction rate approaches steady value around 0.035 [reacted CO(mol)/gcat/h] above value of the product of two properties around 6 as shown in Fig. 3. The approach to constant rate is mainly attributed to fast methanol dehydration rate to DME on acidic sites compared to CO hydrogenation rate to methanol on copper surfaces [13,19]. Although copper surface area could be significantly enhanced by forming small particle size of copper, the reaction rate is not sufficiently increased due to the small increase of the total amount of acidic sites on bifunctional catalysts. The smaller acidic sites with high surface area of metallic copper (small particle size) is mainly induced by acidic site blockage on Al_2O_3 or Zr-modified ferrierite catalysts by the possible deposition of small Cu-ZnO-(Al_2O_3) particles, which results to show a lower reaction rate. Therefore, the quantity of the acidic sites is more crucial factor to obtain a high DME yield on the bifunctional catalysts than the surface area of metallic copper. Interestingly, TOF values are larger on bifunctional catalysts which showing small values of (copper surface area \times amount of acidic sites), and TOF values decrease around 0.10 [reacted CO molecules/surface Cu atom/s] up to 3 of the product values of two properties. However, further increase of copper surface area shows no significant variation of TOF values and it is kept at constant value of around 0.10. The results suggest that the direct DME synthesis from syngas on the bifunctional catalysts is not structure-sensitive reaction, and high DME yield could be obtained by simply controlling the amounts of copper surface area and acidic sites by forming proper size of Cu-ZnO-(Al_2O_3) particles on solid acid catalyst surface by retaining a large amount of acidic sites. The fast methanol dehydration rate to DME compared to CO hydrogenation rate to methanol also reveals that the amount of acidic sites and their strength (from the results of NH_3 -TPD) is more crucial factor than copper surface area for

obtaining a high DME yield. Furthermore, the rate of surplus hydrogen formation could be accelerated by increasing DME formation with a concomitant increase of equilibrium conversion of CO.

4. Conclusions

The catalytic performances on the bifunctional catalysts for direct DME synthesis from biomass-derived syngas are strongly related with the amount of acidic sites with surface area of metallic copper, and it is mainly due to the fast rate of methanol dehydration to DME compared to that of CO hydrogenation to methanol. Even though the high activity for methanol synthesis by designing a high surface area of metallic copper with a low aggregation character is important, the amount of acidic sites is more crucial factor to obtain a high DME yield from syngas than the surface area of metallic copper on the bifunctional catalysts. The values of (copper surface area (m^2/g) \times amount of acidic sites ($\text{mmol NH}_3/\text{g}$)) are well correlated in the shape of inverse-exponential curve with CO conversion and DME yield, and the correlation is mainly due to the increased metallic copper surface area and the amount of acidic sites together on this consecutive reaction. In addition, the reaction rate for direct DME synthesis from syngas approaches to some constant reaction rate, and it is also attributed to the fast methanol dehydration rate to DME on acidic sites compared to that of CO hydrogenation to methanol on the exposed copper surfaces by shifting an equilibrium conversion of CO. TOF values of direct DME synthesis from syngas on bifunctional catalysts are decreased up to the value of 3 (copper surface area \times amount of acidic site), and the value approaches to 0.10 [reacted CO molecules/surface Cu atom/s] above the value of 3 due to the possible blockage of acidic sites by small Cu-ZnO-(Al_2O_3) particles.

Acknowledgement

The authors would like to acknowledge the financial support from the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST; 2011-0009003 and 2012-0001387).

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